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The Entropy of the Square-Well Fluid

I. The Random Phase Approximation

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Abstract

The analytical expression of the entropy is obtained for the square-well fluid within the random phase approximation.

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In a general case the entropy of an equilibrium system, *S*, is (hereafter, all thermodynamic quantities are taken per atom) (see, for example, [1]):

$$S = S_{\mathrm{IG}} - \frac{1}{2} k_{\mathrm{B}} \rho^2 \int\int g^{(2)}(\bar{r_1}, \bar{r_2}) \ln\left[g^{(2)}(\bar{r_1}, \bar{r_2})\right] \mathrm{d}\bar{r_1} \mathrm{d}\bar{r_2} -$$

$$-\frac{1}{6}k_{\mathrm{B}}\rho^3\iiint g^{(3)}(\bar{r_1},\bar{r_2},\bar{r_3})\ln\left[\frac{g^{(3)}(\bar{r_1},\bar{r_2},\bar{r_3})}{g^{(2)}(r_1,r_2)g^{(2)}(r_1,r_3)g^{(2)}(r_2,r_3)}\right]\mathrm{d}\bar{r_1}\mathrm{d}\bar{r_2}\mathrm{d}\bar{r_3}-.....\quad(1)$$

where S_{IG} is the entropy of the ideal gas (IG), ρ - mean atomic density, $g(r)=g^{(2)}(|\bar{r_1}-\bar{r_2}|)$ - pair correlation function, $g^{(3)}(\bar{r_1},\bar{r_2},\bar{r_3})$ - three-particle correlation function, k_{B} - Boltzmann constant. Eq.(1) is not useful in practice.

If expressions for pressure or internal energy are known, the entropy can be found [1] by integrating one of the following relations:

$$-\rho^2\left(\frac{\partial S}{\partial\rho}\right)_\rho=\left(\frac{\partial P}{\partial T}\right)_\rho\ ,\qquad(2)$$

$$\left(\frac{\partial S}{\partial T}\right)_\rho=\frac{1}{T}\left(\frac{\partial\left(K+U\right)}{\partial T}\right)_\rho\ ,\qquad(3)$$

where T is the absolute temperature, P – pressure, K - kinetic energy, U - potential energy. In the pair-interaction approximation

$$U=2\pi\rho\int_0^\infty\varphi(r)g(r)r^2\mathrm{d}r\ ,\qquad(4)$$

where $\varphi(r)$ is the pair interatomic potential.

To obtain the IG entropy, eq.(3) can be used taking into account that $U_{\mathrm{IG}}=0$. For the hard-sphere (HS) model eq.(3) is not applicable since expression under integral sign is singular and therefore it is necessary to use eq.(2) to obtain an additional HS term to S_{IG}, ΔS_{HS},. The difference between S_{HS} and the entropy of the square-well (SW) fluid can be found again from eq.(3).

The SW model is determined by means the following pair potential:

$$\varphi_{\mathrm{SW}}(r)=\begin{cases}\infty, & r<\sigma\\ \varepsilon, & \sigma\le r<\lambda\sigma\\ 0, & r\ge\lambda\sigma\end{cases}\ ,\qquad(5)$$

where ε, λ and σ are the SW parameters.

In the q space

$$U_{\mathrm{SW}}=\frac{2}{3}\pi\rho\sigma^3\varepsilon(\lambda^3-1)+\frac{1}{4\pi^2}\int_0^\infty\left[a_{\mathrm{SW}}(q)-1\right]\phi_{\mathrm{SW}}(q)q^2\mathrm{d}q\ ,\qquad(6)$$

where

$$\phi_{\mathrm{SW}}(q)=\frac{4\pi\varepsilon}{q^3}4\pi\varepsilon\left[\sin(q\lambda\sigma)-\sin(q\sigma)-q\lambda\sigma\cos(q\lambda\sigma)+q\sigma\cos(q\sigma)\right]\ ,\qquad(7)$$

$a_{\mathrm{SW}}(q)$ is the structure factor of the SW system. Within the random phase approximation (RPA) [2] it is written as

$$a_{\mathrm{SW\text{-}RPA}}(q)=\frac{1}{1-\rho c_{\mathrm{HS}}(q)+\beta\rho\phi_{\mathrm{SW}}(q)}\ ,\qquad(8)$$

where $\beta = (k_B T)^{-1}$, $c_{HS}(r)$ is the direct correlation function of the HS fluid related to the HS structure factor as follows:

$$a_{HS}(q) = \frac{1}{1 - \rho c_{HS}(q)} \quad . \tag{9}$$

Then

$$\left(\frac{\partial U_{SW\text{-}RPA}}{\partial T}\right)_\rho = \frac{\rho k_B}{4\pi^2} \int_0^\infty \frac{\phi_{SW}^2(q) q^2 dq}{\left[k_B T (1 - \rho c_{HS}(q)) + \rho \phi_{SW}(q)\right]^2} \quad , \tag{10}$$

$$S_{SW\text{-}RPA} = S_{HS} + \int \frac{dT}{T} \left(\frac{\partial U_{SW\text{-}RPA}}{\partial T}\right)_\rho = S_{HS} + \frac{k_B \rho}{4\pi^2} \text{x}$$

$$\text{x} \int_0^\infty \left[-\frac{1}{\rho^2 \phi_{SW}^2(q)} \left(\ln \left| \frac{k_B}{a_{SW-RPA}(q)} \right| + (1 - \rho c_{HS}(q)) a_{SW-RPA}(q) \right) + \text{Const} \right] \phi_{SW}^2(q) q^2 dq \, . \tag{11}$$

The integration constant is being obtained from the condition that $S_{SW} = S_{HS}$ at $a_{SW\text{-}RPA}(q) = a_{HS}(q)$:

$$\text{Const} = \frac{1}{\rho^2 \phi_{SW}^2(q)} \left(\ln \frac{k_B}{a_{HS}(q)} + 1 \right) \quad . \tag{12}$$

Eq. (11) can be simplified and the final expression is

$$S_{SW\text{-}RPA} = S_{HS} + \frac{k_B}{4\pi^2} \int_0^\infty q^2 \left(\beta a_{SW\text{-}RPA}(q) \phi_{SW}(q) + \frac{1}{\rho} \ln \frac{a_{SW\text{-}RPA}(q)}{a_{HS}(q)} \right) dq \quad . \tag{13}$$

Eq.(12) can be regarded the analytical expression if to use the analytical form for $c_{HS}(q)$ obtained in [3, 4].

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